Intramolecular Hydrogen Bonding in a Triangular Dithiazolyl-Azaindole for Efficient Photoreactivity in Polar and Nonpolar Solvents

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A triangular dithiazolyl-azaindole derivative has been synthesized as a highly sensitive photochromic molecule. 2,4-Dimethyl-5-phenylthiazol derivative 1a, and a reference compound, 5-methyl-2-phenylthiophene derivative 2a, both showed photochromism with quantum yields of 90 and 45%, respectively, in hexane, and 90 and 35%, respectively, in methanol. In the single-crystal state, **1a** revealed photochromic coloration. Its conformation was assigned to a photoreac-

Introduction

Photoresponsive molecules have been developed to manipulate the chemical and physical properties of various molecules and polymers and are widely used in many practical applications.^[1] Recently, particular interest has focused on photochromic molecules as an active unit for photo-reversible control of various molecular properties such as color,^[2-4] fluorescence,^[5-9] electrochemistry,^[10,11] chemical reactivity,^[12] and magnetism.^[13] Among a number of photochromic molecules, those based on a hexatriene backbone, such as diarylethenes^[14] and fluguides,^[15] have attracted broad attention because of their persistent photochromic nature; such molecules do not undergo spontaneous isomerization reaction under dark conditions. A wide range of possible chemical modifications of diarylethene, in particular, have been demonstrated, which has stimulated further synthetic chemistry on this class of molecules. The photochemical reactivity of various photochromic diarylethenes and their derivatives has been studied to elaborate structure-reactivity relationships.^[14a] Because the photochromic reaction leading from the hexatriene structure to the cyclohexadiene structure proceeds with contra-rotational motion of the reactive carbons, a C_2 -symmetric geometry around the hexatriene reaction center is required for high sensitivity.^[16,17] Complete control of molecular conformation has been achieved in some crystalline samples of diarylethenes, which have been reported to show almost

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tive state with C_2 -symmetry around the hexatriene reaction center. Temperature-dependent NMR studies and quantum chemical calculations indicated the contribution of intramolecular hydrogen-bonding between the central azaindole unit and the side thiazole units, which stabilizes the photoreactive C_2 -symmetric conformation and elevates the photoreactivity in both non-polar and polar solvents.

100% photochromic quantum yield. This has stimulated a number of synthetic works on hexatriene-type photochromic molecules with high sensitivity in solution phase. Recently, we have been exploring photochromic terarylenes in which three aromatic units are connected in a triangular manner, forming a hexatriene backbone.^[12a,18] Some heteroaromatic units possessing hydrogen-bonding activity have been introduced as a component of the terarylene structure. The authors recently reported that a dithiazolylbenzothiophene derivative shows a photon-quantitative reaction with almost 100% photocyclization quantum yield.^[19] This extremely high photochromic reactivity of the molecule was explained in terms of specific intramolecular S/N and CH/N non-covalent interactions, which were thought to stabilize the C_2 -symmetric conformation in nonpolar solvents. In the field of supramolecular chemistry, intramolecular and inter-arylene unit interactions have been developed to regulate the rotational configuration of oligoarylene molecules forming specific foldamers.^[20]

We herein expand our study and introduce an N-methylazaindole unit as a central bridging unit in the terarylene structure. Although the photocyclization quantum yield of diarylethene derivatives is usually suppressed in polar solvents because of specific twisted intramolecular charge transfer (TICT)^[21] in the excited state, the present molecule exhibits photocyclization quantum yield as high as 90% in methanol.

Results and Discussion

2,3-Dithiazolylazaindole 1a (Scheme 1) was designed as a representative photochromic molecule in which the molecular conformation was expected to be stabilized in the photo-reactive conformation through intramolecular hy-

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FULL PAPER

drogen-bonding, as depicted by dotted lines in Scheme 1. The weak CH/N hydrogen-bonding^[22] could tether the side thiazolyl rings to the bridging azaindole unit. These interactions are expected to stabilize co-planar structures whereas steric hindrance operating between the methyl groups on both thiazole units twist the thiazolyl rings. The methyl groups are able to interact with the thiazole rings on the opposite site through CH– π interactions. A molecular conformation with C_2 -symmetry around the hexatriene moiety was thus expected to be stable. 2,3-Dithienylazaindole **2a** was also designed as a reference compound in which the nitrogen atoms in the thiazole rings were replaced by CH units.



Scheme 1. Photochemical and thermal interconversions of terarylenes 1–3.

2,3-Diarylazaindoles **1a** and **2a** were synthesized by conventional cross-coupling reactions from the corresponding arylene units. Their chemical structures were confirmed with high-resolution mass spectroscopy, ¹H NMR, and ¹³C NMR analyses as well as by X-ray single-crystal analysis. Detailed procedures and characterization data are presented in the experimental section.

As shown in Figure 1, compounds 1a and 2a showed photochromic profiles similar to those of previously reported terarylenes and diarylethenes. Because isosbestic points were clearly observed, these spectral changes can be attributed to a two-component photochromic reaction. The colored solutions were bleached upon visible light irradiation with a wavelength longer than 400 nm. The colored component **1b**, formed after UV light irradiation of a hexane solution of 1a, was isolated by reversed-phase HPLC purification. The closed-ring isomer 1b was confirmed by MS and ¹H NMR spectroscopy in CDCl₃ solution. Visible light irradiation of a solution of **1b** progressively decreased the absorption band at 650 nm, finally giving the absorption spectrum of 1a (Figure 1, a, bold line). The absorption band in the visible range again increased upon UV irradiation ($\lambda = 313$ nm) to reach a photostationary state (PSS, gray line). The conversion ratio between the colorless and colored isomers at PSS was estimated to be more than 95%.

The colored solution of compound **2** after UV light irradiation showed spontaneous bleaching under ambient conditions, probably due to steric repulsion between the *N*methyl group at the central azaindole and the proton at the side thiophene in the ring-closed form. The colored compound derived from **2a** therefore could not be separated from the colored solution. Nevertheless, the colored form is regarded as the cyclohexadiene form **2b**, illustrated in Scheme 1, because (1) clear isosbestic points were observed, (2) the colored solution showed a specific absorption band at 680 nm typical for the ring-closed form of isomers of terarylene and diarylethenes, and (3) TD-DFT calculations for **2b** are in agreement with the observed absorption bands at 400 and 710 nm.^[23]



Figure 1. Absorption spectral changes of 1 (a) and 2 (b) in hexane. Open-form **a** (bold lines), closed-form **b** (dotted line for 1), and photo-stationary state under irradiation with 313 nm light (gray lines). The concentrations of 1 and 2 were 4.2×10^{-5} and 2.0×10^{-5} M, respectively.

The thermal stability of the closed-ring isomers **1b** and **2b** was then investigated. Compound **1b** showed negligible thermal cycloreversion reaction under dark conditions at room temperature, and exhibited spontaneous bleaching with a half-life time of about one month at 333 K. In contrast, **2b** showed single exponential bleach kinetics under ambient conditions, and the half-life time in hexane was about 5 h at room temperature.

We successfully obtained a macroscopic crystal of compound **1a** from a hexane solution, and its photochromic properties in the single-crystal state were studied.^[24] The single-crystal of **1a** became green upon UV light irradiation and was bleached under visible light irradiation. This coloration and bleaching cycle could be repeated more than 20 times with no obvious degradation; the observed color change, is shown in Figure 2 (a and b). Part c of Figure 2 shows the polarized absorption spectra of the crystal in the colored state. The reversible appearance and disappearance of an absorption band at approximately 650 nm indicated photochromic reactions between **1a** and **1b** in the crystal state. The specific polarization in this absorption band, and its sustention upon coloration–bleaching cycles suggest that the molecular alignment in the crystal lattice is maintained during the photo-isomerization reactions.^[25]



Figure 2. Photographs of a crystal of 1 (a) before and (b) after irradiation with UV light. (c) Polarized absorption spectra of the photo-generated green crystal of 1.

The ORTEP drawing of 1a shown in Figure 3 displays the conformation of C_2 -symmetry around the central hexatriene moiety. Regarding the contra-rotational motion in the hexatriene moiety upon photocyclization, the C_2 -symmetric structure seems to be suitable for the photochromic reaction, which is typically recognized as an anti-parallel conformation of the diarylethene. The distance between the reaction center carbon atoms, C11 and C21, in the thiazole units was about 3.5 Å, which is short enough for the photocyclization reaction to take place in the hexatriene unit.^[26] The X-ray structural data also provides information on the intramolecular atomic contact interactions. Interatomic distances between the N4/H1 atoms and the N3/H6 atoms were estimated to be 2.70 Å and 2.7 Å, respectively, which are similar to, or a little less than, the sum of the van der Waals radii of the H (1.2 Å) and N (1.55 Å) atoms. These atomic contacts clearly indicate dual intramolecular hydrogen-bonding interactions between the nitrogen atoms and the CH units. Similar multiple hydrogen-bonding interactions have been reported to control rotational isomerization of polyarylene molecules that form specific foldamer structures.[27]

Quantum chemical calculations based on the density functional theory $(DFT)^{[28]}$ at the B3LYP/6-31G* level were performed to evaluate an optimized structure of **1a**, as shown in Figure 4. The coplanar optimized molecular structure was evaluated with the C_2 -symmetric hexatriene reaction center, in which the distance between the reactive carbon atoms was as short as 3.69 Å. This evaluated structure



Figure 3. ORTEP drawing of the open-ring isomer in crystal **1a**, showing 50% probability displacement ellipsoids.

ture was similar to the ORTEP structure obtained from the X-ray analysis and appears to be suitable for the photocyclization reaction. The atomic contacts between H1 and N4, and between H6 and N3 (estimated distance; H1/N4: 2.9 Å and H6/N3: 2.6 Å) were well-reproduced in the DFT calculation. The CH/N intramolecular interactions were also supported by the calculation. The distance between the methyl protons on the thiazole units and the molecular planes of the opposite thiazole units were evaluated to be approximately 3.2 and 3.3 Å for each of the molecule sides, which are also short enough to allow CH/ π interactions.



Figure 4. Optimized structures at the B3LYP/6-31G* level; (a) **1a** and (b) **1b**. Left side: overall view; Right side: side-view of the area associated with hydrogen-bonding interactions.

To evaluate the conformation of **1a** in solution, the temperature dependence of ¹H NMR spectra were studied in [D₈]toluene and [D₄]methanol. The ¹H NMR signal of H1 on the 1-methyl-7-azaindole unit of **1a** (see Figure 3) was observed at $\delta = 8.25$ ppm at 293 K as a double-doublet signal (J = 7.5, 1.3 Hz) in [D₈]toluene, as shown in Figure 5. The chemical shift was far downfield compared to that of the corresponding proton in compound **2a** ($\delta = 7.72$ ppm).^[23] Such a downfield shift has been reported as a typical feature of intramolecular weak CH/N hydrogenbonding.^[29] As summarized in Figure 6, the chemical shift of H1 showed a systematic upfield shift of 0.095 ppm upon

FULL PAPER

heating from 293 to 353 K. Furthermore, the signal corresponding to the N-methyl protons of 1-methyl-7-azaindole in compound 1a showed an upfield shift upon heating from 293 to 353 K, which also suggests specific hydrogen-bonding at room temperature. No other signal from the 1methyl-7-azaindole group revealed such a significant temperature dependence. In contrast, signals of the H1 and Nmethyl protons on the 1-methyl-7-azaindole group in compound 2a showed a slight downfield shift upon heating to 353 K. These results indicate that the CH/N interactions in compound 1a are attenuated at higher temperatures and that the molecular conformation changes upon heating. That is, at higher temperature, the distance between the hydrogen and nitrogen atoms and the twisting angle between the 1-methyl-7-azaindole group and the thiazole unit become larger. As also shown in Figure 5, signals of the methyl groups at the reactive carbon atoms of the thiazole rings of **1a** were observed at $\delta = 1.89$ and 1.82 ppm at 293 K. Systematic downfield shifts of these peaks upon heating indicates a suppressed reverse ring-current effect at higher temperature. Thus, the temperature dependence of these signals is also consistent with a planar geometry at room temperature and a larger twisting angle at higher temperatures. In [D₄]methanol solution, ¹H NMR signals of H1 and N-methyl protons in compound 1a also showed similar upfield shifts upon heating (shown in Figure 6). Thus, intramolecular hydrogen-bonding seems to be effective even in methanolic solutions of compound 1a. It should be noted that the N-methyl signal in $[D_4]$ methanol indicated almost the same temperature dependence as that in toluene, whereas the H1 signal showed suppressed temperature dependence in methanol.



Figure 5. Temperature-dependent ${}^{1}H$ NMR spectra of 1a in [D₈]-toluene.

Finally, we report on the photochromic properties of compounds 1 and 2, which are summarized in Table 1. The photochromic reaction quantum yields of 1 were measured with the standard procedure using 1,2-bis(2-methylbenzo-[b]thiophen-3-yl)perfluorocyclopentene^[30] and 1,2-bis(2,3-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene^[31] as reference compounds for photocyclization and cycloreversion reactions, respectively. On the other hand, the photochromic reaction quantum yields of 2 were evaluated by numerical fitting of the progression curve of the absorption band corresponding to the ring-closed isomer **2b** as a func-



Figure 6. Temperature-dependent chemical shifts of (a) H1 and (b) N-methyl protons of **1a** in $[D_8]$ toluene and in $[D_4]$ methanol and **2a** in toluene.

tion of UV irradiation time due to the spontaneous thermal bleaching.^[23] Because this procedure also needed an estimate of the absorption coefficient, the calculated values appear to include significant probable error for 2b as compared to those estimated from the standard procedure. The photocyclization quantum yield, Φ_{a-b} , of **1a** was 90% in hexane and also in methanol, whereas those of 2a were less than one half of those of **1a**. Because the dynamics of the photocyclization reaction of diarylethene proceeds within less than 200 fs, its photochromic quantum yield is mainly affected by the thermal equilibrium in the ground state and not in the excited state. That is, the extremely high quantum yield of 1a should require a significantly high population ratio of the reactive C_2 -symmetric conformation in the solution phase, which would be promoted by the tight dual CH/ N interactions in both hexane and methanol.

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of 1-3, together with the quantum yields in solution.

	$\lambda_{\rm max} \ [{\rm nm}] \ (\epsilon \ [10^4 \ {\rm m}^{-1} \ {\rm cm}^{-1}])$	$arPsi_{ m a-b}$	$\Phi_{\mathrm{b-a}}$
1 a 1 b 2 a 2 b 3 a	297 (3.0) 654 (1.0) 294 (3.5) 680 (1.0 ^[c]) 307 (2.9)	$\begin{array}{c} 0.90,^{[a]} \ 0.90^{[b]} \\ - \\ 0.45,^{[a][c]} \ 0.35^{[b][c]} \\ - \\ 0.98,^{[a]} \ 0.54^{[b]} \end{array}$	- 0.007 ^[a] - 0.086 ^{[a][c]} 0.008 ^[a]
		•	

[a] In hexane. [b] In methanol. [c] Calculated.

We herein briefly comment on a comparison between the photochromic quantum yields of 1a and 3a, the photocyclization quantum yields of which have recently been reported to be 98% in hexane and 54% in methanol.^[19] Because both molecules are composed of similar molecular units and display dual non-covalent intramolecular interactions, one may expect similar photochromic reactivity. Indeed, the photochromic quantum yield of 1a was similar to that of 3a in hexane (90% for 1a and 98% for 3a), whereas that of **3a** was significantly suppressed in methanol. The difference between Φ_{a-b} of the two compounds in methanol suggests that the CH/N interaction in 1a might be stronger than the S/N interaction in 3a, and that the reactive C_2 -symmetric conformation of 1a persists even in methanol. In methanolic solution, 3a showed no marked temperature-dependent ¹H NMR shifts, and almost no specific regulation of conformation with the intramolecular interaction. In hexane, both 1a and 3a are mostly in the reactive conformation and show high Φ_{a-b} . A slight difference in Φ_{a-b} of **1a** (Φ_{a-b} = 0.90), and of **3a** (Φ_{a-b} = 0.98), may thus be explained, not from the viewpoint of population ratio of the reactive and non-reactive conformations, but by the reactivity of the reactive conformation. Regarding this minor contradiction, little attention was paid to the distance between the N1- CH_3 and N3 atoms in 1a and in 1b, which were evaluated by the DFT calculations to be 0.261 and 0.282 nm, respectively (see Figure 4). The H6/N3 distance in 1b is longer than the sum of the van der Waals radii of hydrogen and nitrogen atoms, which suggests that the N1-CH₃/N3 interaction is not effective in 1b. Collapse of the CH₃/N3 interaction upon the photocyclization of **1a** to **1b** should require excess heat for the reaction and could be the origin of decreased photocyclization reactivity of **1a**. Meanwhile, the distance between the N1-CH₃ unit and the N2 atom on the azaindole unit in 1a and 1b was demonstrated to be 0.246 and 0.247 nm, respectively, indicating a tight interaction between these moieties both before and after the photocyclization. As a result of this intra-unit tight CH/N interaction, the H6 atom is out of the molecular plane of the azaindole unit, and the distance between the H6 and the N3 atoms is short in the twisted 1a but not in the coplanar 1b. This specific stabilization of the reactive conformation of 1a with the intramolecular non-covalent interaction could be the origin of the slightly suppressed photochromic reactivity of 1a compared with that of 3a for which the S/N interaction should be effective for both the open and the closed forms. To gain further understanding, the authors are now exploring X-ray structural analyses of the closed ring isomers 1b and 3b.

Conclusions

We have designed and synthesized diarylazaindole derivatives **1a** and **2a**. The former was designed as a representative photochromic molecule with intramolecular hydrogenbonding between the central azaiodole unit and the side thiazole units. The photocyclization quantum yields of



compound 1 in hexane and in methanol were 0.90, whereas those of compound 2 in hexane and in methanol were estimated to be 0.45 and 0.35, respectively. Compound 1a is stabilized in the reactive conformation with C_2 -symmetry through dual intramolecular hydrogen-bonding, as revealed by both X-ray crystal structure analysis and DFT calculations. Intramolecular hydrogen-bonding in the solution phase was also supported by the results of temperature-dependent ¹H NMR spectroscopic studies.

Experimental Section

General: ¹H NMR spectra were recorded with a JEOL AL-300 spectrometer (300 MHz). Preparative HPLC was performed with a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus Series. Mass spectra were measured with a JEOL JMS-T100LC AccuTOF mass spectrometer instrument. Absorption spectra in solution were studied with JASCO V-550 and V-670 spectrophotometers with a temperature control unit. Photoirradiation was carried out using an USHIO 500 W ultra-high-pressure mercury lamp or a Panasonic Aicure UV curing system (LED, λ = 365 nm) as the excitation light source. Monochromic light was obtained by passing the light through a monochromator (Shimazu SPG-120S, 120 mm, f = 3.5). Absorption spectra in the single-crystalline phase were measured by using an Olympus BX-51 polarizing microscope connected to a Hamamatsu PMA-11 photodetector through an optical fiber; polarizer and analyzer were set in parallel. X-ray crystallographic analyses were carried out with a Rigaku R-AXIS RAPID/s Imaging Plate diffractometer with Mo- K_{α} radiation at 296 K.

Syntheses of Compounds 1a and 2a: Compounds 1a and 2a were prepared with cross-coupling reactions as illustrated in Scheme 2.



Scheme 2. Syntheses of compounds 1a and 2a. Reagents and conditions: K_2CO_3 , $P(aTol)_3$, $Pd(OAc)_2$, anhydrous DMF.

1-Methyl-2,3-bis(5-methyl-2-phenylthiazol-4-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (1a): A mixture of 2,3-dibromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (4; 0.12 g, 0.4 mmol),^[32] 5 (0.31 g, 1.0 mmol), Pd(OAc)₂ (9.8 mg, 0.04 mmol), tri(o-Tolyl)phosphane [P(oTol)₃; 28 mg, 0.09 mmol], and K₂CO₃ (0.67 g 4.8 mmol) in a 100-mL four-necked flask was flushed with nitrogen for 10 min. A solution of DMF (30 mL) was added by syringe and the mixture was heated at 100 °C for 15 h under nitrogen. The cooled reaction mixture was extracted with diethyl ether and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/ethyl acetate, 9:1) and reversed-phase HPLC (methanol) afforded compound **1a** (0.05 g, 0.10 mmol, 25%) as a white solid. ¹H NMR (300 MHz, CDCl₃/TMS): δ = 8.46–8.44 (dd, J = 4.8, 1.5 Hz, 1 H), 8.18–8.16 (dd, J = 7.8, 1.5 Hz, 1 H), 7.98–7.96 (m, 4 H), 7.48–7.41 (m, 6 H), 7.18–7.16 (q, J = 4.8 Hz, 1 H), 3.99 (s, 3 H), 2.02 (s, 3 H), 1.95 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃/TMS): δ = 164.92, 164.24, 148.58, 146.74, 144.01, 143.48, 134.77, 133.92, 133.50, 131.84, 130.08, 129.56, 129.11, 129.08, 129.02, 128.86, 126.29, 126.25, 126.16, 120.24, 116.45, 108.85, 29.84, 12.08, 11.95 ppm. HRMS (FAB): calcd. for C₂₈H₂₂N₄S₂+[M]⁺ 478.1286; found 478.1288. C₂₆H₂₂N₄S₂ (454.61): calcd. C 70.26, H 4.63, N 11.71; found C 70.00, H 4.53, N 11.53.

Compound 1b: ¹H NMR (300 MHz, CDCl₃/TMS): δ = 8.14–8.09 (m, 2 H), 8.01–7.98 (m, 2 H), 7.88–7.85 (m, 2 H), 7.54–7.26 (m, 6 H), 6.84–6.81 (q, *J* = 4.5 Hz, 1 H), 3.86 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H) ppm.

1-Methyl-2,3-bis(2-methyl-5-phenylthiophen-3-yl)-1H-pyrrolo[2,3-b]pyridine (2a): Prepared by the same procedure as that used for 1a. except that 5 was replaced by 2-methyl-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (6). From 4 (0.15 g, 0.5 mmol) and 6 (0.34 g, 1.0 mmol) with $Pd(OAc)_2$ (8.0 mg, 0.04 mmol), P(oTol)₃ (14 mg, 0.05 mmol), and K₂CO₃ (0.67 g, 4.8 mmol) in DMF (40 mL), 2a (0.018 g, 0.04 mmol, 8.0%) was obtained as a white solid. ¹H NMR (300 MHz, CDCl₃/TMS): δ = 8.43–8.40 (dd, J = 4.8, 1.5 Hz, 1 H), 7.93–7.89 (dd, J = 7.8, 1.5 Hz, 1 H), 7.60–7.56 (d, J = 7.2 Hz, 2 H), 7.54–7.51 (d, J = 7.2 Hz, 2 H), 7.42-7.22 (m, 7 H), 7.17-7.12 (m, 2 H), 3.86 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃/TMS): δ = 148.25, 143.14, 140.98, 139.95, 139.39, 134.82, 134.47, 133.94, 133.41, 131.84, 128.96, 128.81, 127.70, 127.51, 127.01, 125.48, 125.35, 124.47, 120.13, 116.08, 109.23, 29.68, 14.28, 14.15 ppm. HRMS (EI): calcd. for $C_{30}H_{24}N_2S_2{}^+$ $[M\ +\ H]^+$ 476.1381; found 476.1381. C₃₀H₂₄N₂S₂+0.4H₂O (476.7+7.2): calcd. C 74.54, H 5.16, N 5.79; found C 74.47, H 4.97, N 5.67.

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- [23] See the Supporting Information.
- [24] Crystallographic data for **1a**: $C_{30}H_{22}S_3$; a = 10.1529(10), b = 11.1215(11), c = 11.4418(10) Å, a = 80.729(2), $\beta = 68.156(2)$, γ

= 79.614(2)°; triclinic, space group $P\bar{I}$; Z = 2; $V = 1173.27(19) Å^3$; $\rho_{calcd.} = 1.355 \text{ g cm}^{-3}$. Of 9720 reflections up to $2\theta = 50.7$, 4295 were independent ($R_{int} = 0.032$) and 3392 were with $I > 2\sigma(I)$. The structure was solved by direct methods and refined with a full-matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. wR = 0.1166, R = 0.0460. CCDC-796948 (for **1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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